AGGLOMERATION OF LOW-RANK COAL AS A PRETREATMENT
FOR DIRECT COAL LIQUEFACTION

G. A. Robbins, R. A. Winschel, C. L. Amos
CONSOLIDATION COAL COMPANY
Research & Development
4000 Brownsville Road
Library, PA 15129

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INTRODUCTION

Oil agglomeration is an effective technique for recovering and deashing coal fines. In addition to conventional uses of oil agglomeration, certain features make it attractive as a pretreatment for coal liquefaction. The small coal grind size required for liquefaction may improve the release of mineral contaminants from the coal. These sizes may be more easily handled by oil agglomeration than by conventional cleaning methods. The use of process-derived oil eliminates the additional cost of the agglomerating oil. It also has been shown that pyrite is not effectively removed from coal fines by oil agglomeration (1), since its surface is readily coated by oil. Pyrite is recognized as a liquefaction catalyst (2) and retention of this mineral can be beneficial in liquefaction processes. The economic incentive for lowering the ash content of liquefaction feedstocks result from: 1) the potential of down-sizing or eliminating deashing equipment, 2) improved yields from more efficient ash rejection, 3) reduced erosion/abrasion of equipment, and 4) slightly improved organic throughputs resulting from reduced ash inventory in the system.

The goal of this work was to determine if coal liquefaction process oils are effective in cleaning low-rank coals (subbituminous and lignite) by agglomeration. Previous work of this nature in this laboratory has been limited to characterization of oils for the agglomeration of bituminous coal (3). The work reported here has been described in complete detail in DOE reports (4,5). The coals tested consisted of three subbituminous coals, a Texas lignite, and a bituminous coal (for comparison and establishing operating conditions). The agglomerating oils included petroleum-derived No. 2 diesel fuel and No. 6 fuel oil, two Lummus Integrated Two-Stage Liquefaction (ITSL) distillates from bituminous coal runs, and a Wilsonville ITSL distillate from a run with Texas lignite. Past bench-scale work at Consol using similar equipment has provided results which were scalable to commercial operation at 40 tph (6).

EXPERIMENTAL

The coals used in the tests are described in Table 1. All coals were run-of-mine; several were supplied previously ground. The agglomerating oils and surfactant are described below, and selected properties are shown in Table 2.

- Diesel Fuel No. 2 - Purchased locally.
- Fuel Oil No. 6 - API gravity 13, low sulfur grade.
- Lummus Run 3LCF9 - A sample of the 500 x 850°F distillate second-stage product produced in October 1982 at the Lummus ITSL PDU during a period of run 3LCF9 using Old Ben No. 1 Mine (Indiana V) coal.
- Lummus Run 3LCF7 - A composite sample of the 850°F⁻ distillate portion of the second-stage heavy-oil product made during Run 3LCF7 of the Lummus ITSL PDU with Old Ben No. 1 Mine (Indiana V) coal.

- Wilsonville Run 255 - A sample of the recycle distillate inventory (V-1074) from 5/2, 4, 6, 7/88 during Run 255, made while the plant processed Martin Lake (Texas) lignite, nominal b.p. about 650 x 1000°F.
- Cresylic Acid No. 83 Black (Merichem Company, Houston, Texas).

Agglomeration experiments were performed in a cylindrical stainless steel vessel (Figure 1). The drive motor is rated at 1700 rev/min. The test procedure is shown in Figure 2. A cylindrical heating mantle was used when tests were made above ambient temperature.

Inversion, or phase separation, was manifested by a distinct change in the sound produced by the mixing action and by changes in color and texture at the surface of the slurry. In some tests, additional oil was added to increase agglomerate size. The reject material was dried at 105°C to constant weight (at least two hours), and then weighed and ashed at 800C to constant weight (three hours or more).

The agglomerates were allowed to air-dry until they were visibly dry (16-48 hours). Moisture and ash were determined on the agglomerated products.

Organic recoveries, ash rejections, and ash balances were determined as shown below:

Organic Recovery =

$$\left[1 - \frac{\text{mass of dry reject - mass of ash in reject}}{\text{mass of MAF coal + mass of oil}}\right] \times 100\% \tag{1}$$

Ash Rejection =

$$\left[\frac{\text{mass of coal ash charged - mass of ash in product}}{\text{mass of coal ash charged}}\right] \times 100\% \tag{2}$$

Ash Balance =

$$\left[\frac{\text{mass (ash) in agglomerates + mass (ash) in dry reject}}{\text{mass of coal ash charged}}\right] \times 100\% \tag{3}$$

Though not determined, oils were assumed to be ash-free for the calculations. The ash balance calculations (Table 3) do not account for any water-soluble ash. However, elemental analyses of products, rejects and water-soluble ash from two runs were used to obtain complete ash elemental balances and rejection selectivities.

RESULTS AND DISCUSSION

General

Results are reported for nineteen successful agglomeration tests performed with six coal samples (lignite through hvAb) and five different agglomerating oils. Unsuccessful trials are described in another report (4), but not presented here. Table 3 gives the conditions and results of all the successful agglomeration trials (i.e., those runs which produced agglomerates). Organic recoveries ranged from 85% to 100% and were greater than 98% for all the low-rank coal tests. Ash rejections ranged from -1% to 72%. The low-rank coal tests gave ash rejections of up to 56%. Ash balances were 73% to 108% (not accounting for water-soluble rejected ash).

After initial work with a variety of coals, efforts were concentrated on Texas lignite and Wyodak subbituminous coal. Of ten tests conducted with Texas lignite, four produced agglomerates with a petroleum oil and one produced agglomerates with a coal liquefaction oil (fortuitously, the lignite-derived oil). Ash rejection with

No. 6 fuel oil ranged from 39 to 56%, while the lignite-derived oil gave 39% ash rejection. Organic recoveries were always greater than 98% and ash balances ranged from 73% to 100%.

Wyodak subbituminous coal was successfully agglomerated with three different coal liquefaction oils and one petroleum-derived oil. Ash rejections with the coal liquefaction oils ranged from 6 to 19%. With No. 6 fuel oil, ash rejections were 1 to 15%. Organic recoveries were about 98% and ash balances ranged from 88 to 102%.

A chart of the coal/oil combinations used appears below.

CHART OF COAL/OIL COMBINATIONS TESTED FOR AGGLOMERATION

Oils	COALS					
	Texas Lignite	Wyodak (Coarse) Subbit.	Wyodak (Fine) Subbit.	Rosebud Subbit.	Kemmerer Subbit.	Pittsburgh Seam Bitum.
Diesel Oil	-	--	----	---	+	++
No. 6 Fuel Oil	++++	+	+	0	0	0
Lummus 3LCF9 Oil	-	+	++	++	+	+
Lummus 3LCF7 Oil	--	+	0	0	0	0
W'ville Run 255	+-	0	+	0	0	0

- = No agglomeration
+ = Agglomeration
0 = No test performed with this combination

The low-rank coals are ranked Kemmerer > Wyodak fine ▪ Wyodak coarse ▪ Rosebud > Texas lignite in terms of ease of agglomeration. Kemmerer coal appears to be equivalent to Pittsburgh seam coal in ease of agglomeration, but the Kemmerer coal had a very low initial ash content and thus gave low ash rejections. There was no difference evident in the response to agglomeration of -200 mesh (finely ground) compared with -28 mesh (coarsely ground) Wyodak coal. Some mineral liberation effect may have been evident, since the coarser grind size gave a maximum ash rejection of 10%, compared to 19% for the finer grind size.

The oils appear to be ranked No. 6 fuel oil > the three coal liquefaction oils > diesel oil in agglomerating ability. Every coal liquefaction oil successfully agglomerated one of the Wyodak coals, but no data are available to directly compare them in agglomeration of other coals. It appears that appropriate agglomeration temperatures for the oils are: room temperature for diesel oil and the two Lummus oils; 38°C for Wilsonville oil; and 54°C for No. 6 fuel oil. Note that no systematic attempt was made to optimize the agglomeration temperature for each oil. Precedent for effective temperatures for No. 6 fuel oil and the two Lummus oils was established in earlier work using bituminous coals (3).

Effects of Promoter and pH

It was reported elsewhere that cresylic acid promoted the agglomeration of lignite (7). Cresylic acid was used as a surfactant or additive in five runs, with the following effects: 1) it was necessary for the agglomeration of the lignite with the lignite-derived oil at the conditions tested (Run 35), 2) it appeared to improve ash rejection (Wyodak subbituminous coal (Runs 23 and 36), but not lignite), 3) it improved the slow kinetics of agglomeration of the lignite, and 4) it lowered the ash balance. In Run 30 (no cresylic acid), the induction period for phase inversion

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was about 40 minutes. In Run 33, with cresylic acid, the induction period was about 6 minutes. Obviously, this has significant consequences for any commercial application of this technology. The lignite is the only coal that was successfully agglomerated which showed any significant kinetic limitation in agglomeration; the other coals had induction periods of two minutes or less. In Run 35, the induction time was about 12 minutes. A similar run made without cresylic acid was terminated after one hour without agglomeration. These results indicate that cresylic acid speeds up the agglomeration of the lignite.

In several agglomeration trials, the pH was adjusted by the addition of various reagents prior to oil addition, without effect in most cases. The one exception was Run 31, in which the slurry pH was adjusted from 6.8 to 2.0 by the addition of HCl. The run was otherwise identical to Run 30. The lower pH resulted in faster agglomeration (phase inversion after 9 minutes instead of 40 minutes), higher ash rejection (56% vs 46%) and a lower ash balance (73% vs 96%). This is very similar to some of the effects caused by the addition of cresylic acid. Note that cresylic acid had no effect on slurry pH.

Elemental Balances

It is necessary to analyze the rejected water (filtrate) to close ash and ash elemental balances. Complete ash and elemental balances were obtained from one agglomeration run with Martin Lake (Texas) lignite (Run 35) and one run with Clovis Point (Wyodak seam) subbituminous coal (Run 35).

Liquid and solid samples were analyzed in duplicate by ICP-atomic emission spectroscopy. Average elemental results were used to calculate a mass balance for ash and for each element. The balances for ash and ash elements relative to the feed coal (i.e., feed coal has 100% of each component) are shown in Figure 3. Ash elemental analyses for the feed coals are given in Table 1. Ash balances shown are on an SO_3-containing and an SO_3-free basis. SO_3 retention is an artifact of the ashing process. The SO_3-free ash balances are a better representation of the coal mineral balances. In coal liquefaction, the fate of the mineral matter is more important than the fate of the ash. For the Wyodak coal test (Run 36), ash rejection was 19.2% (whole-ash and SO_3-free ash bases). For the lignite test (Run 35), the ash rejection was 38.7% (SO_3-containing basis) and 44.3% (SO_3-free basis). This suggests that SO_3-free ash rejections may be uniformly greater than the whole-ash rejections reported for the lignite tests. This results from the selective retention of Ca (and hence SO_3) in the product from the lignite run. Except for ash and ash SO_3, all other components yield the same rejection results when treated on either basis. Overall ash balances were 93 to 96%. Ash balances for individual elements ranged from 89 to 113% for Run 35 and from 84 to 125% for Run 36. The balance for Na_2O was the highest (113% and 125%) observed. Other elements gave balances lower than 106%, with most in the 89 to 96% range. Sodium was greatly reduced in the product agglomerates, and most of it ended up in the water.

Shown in Figure 4 is the selectivity for rejection of each of the ash elements, computed on an SO_3-free basis, for each of the runs. Selectivity was obtained by:

$$\text{Selectivity for Rejection} = \frac{\text{wt oxide in product}}{\text{wt oxide in feed}} \times \frac{\text{wt ash in feed}}{\text{wt ash in product}} \times 100\% \qquad (4)$$

The values thus obtained are less than 100% for components selectively rejected from the product (i.e., rejected to a greater degree than the overall ash) and greater than 100% for components selectively retained in the product. It is evident that Al_2O_3, TiO_2, Fe_2O_3, CaO and MgO were selectively retained in the products and SiO_2 and Na_2O were selectively rejected from the projects in both runs, although retention of Fe_2O_3, CaO and MgO was small in Run 36 (Wyodak). K_2O was rejected and P_2O_5 retained in Run 35 (lignite), but no selectivity for either was observed in Run 36

(Wyodak). Also, ash SO$_3$ was retained in Run 35 (lignite), but showed no selectivity in Run 36 (Wyodak). The fates of the ash elements are clearly illustrated in Figures 3 and 4.

CONCLUSIONS

This work demonstrated that low-rank coals can be cleaned by agglomeration with coal liquefaction oils. To the authors' knowledge, this is the first time cleaning of low-rank coal by agglomeration with coal liquefaction oils has been demonstrated. It is expected that agglomeration performance, e.g., ash rejection and induction time could be further improved by additional testing.

The Texas lignite is readily cleaned by oil agglomeration, with ash rejections of 50% and higher possible. The Wyodak and Kemmerer coals used here appear less amenable to cleaning by agglomeration, the best ash rejections being about 15 to 20%. The Kemmerer coal may have been particularly difficulty to deash because of its low original ash content (3.6%). Rosebud coal showed little or no cleanability under the conditions used; however, the conditions may have been less than ideal.

Each of the coal liquefaction oils tested agglomerated at least one of the Wyodak coals. The apparent ranking of the coals in ease of agglomeration (not necessarily deashing) is Pittsburgh Seam = Kemmerer > Wyodak fine = Wyodak coarse = Rosebud > lignite. The apparent ranking of the oils in agglomerating ability (but not deashing) is fuel oil No. 6 > the three coal liquefaction oils > diesel oil.

Ash elemental results show some form of iron, a potential liquefaction catalyst, is selectively retained in the agglomeration products. also selectively retained are the elements Ti, Ca and Mg. Sodium, a potential poison to supported catalysts is selectively rejected. The concentrations of all ash elements, even those that were selectively retained, are lower in the agglomerated product than in the feed coal.

ACKNOWLEDGMENTS

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TABLE 1

FEED COAL IDENTIFICATION AND ANALYSES COAL/OIL AGGLOMERATION

Designation	Code	Mine	Seam	State	Apparent Rank	Moisture wt %, as det.	Ash, wt % MF
Pittsburgh Seam	MC	--	Pittsburgh	WV	hvAb	1.39	26.15
Wyodak (Coarse)	WC	Clovis Point	Upper & Lower Wyodak	WY	sub.	24.6	8.35
Wyodak (Fine)	WF	Clovis Point	Upper & Lower Wyodak	WY	sub.	20.8	8.41
Kemmerer	KC	Kemmerer	Adaville	WY	sub.	17.9	3.55
Texas Lignite	TC	Martin Lake	Wilcox	TX	lig.	25.9	15.4
Rosebud	RC	Rosebud	Rosebud	MT	sub.	22.98	7.41

Major Elements, Oxide wt % of Ash (As Determined)										
SiO2	Al2O3	TiO2	Fe2O3	CaO	MgO	Na2O	K2O	P2O5	SO3	Unac-counted
Texas Lignite										
50.09	13.51	1.10	4.45	13.12	3.14	1.00	0.62	0.15	13.36	-0.54
Wyodak (Fine)										
28.88	13.32	0.70	6.46	22.60	3.80	1.67	0.25	0.70	22.06	-0.44

Notes and Code: Samples WC, WF, KC, TC and RC supplied by the Wilsonville pilot plant laboratory.
Sample MC supplied by Consol.
Sample WF supplied as -200 mesh.
Samples MC, WC, KC, TC and RC supplied as chunks, ground at Consol to -28 mesh.
Ash elemental analyses were not obtained from coals MC, WC, KC and RC.

TABLE 2

SPECIFIC GRAVITIES AND ^{1}H-NMR PROTON DISTRIBUTIONS OF AGGLOMERATION OILS AND ADDITIVE

Oil Designation	Specific Gravity	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
No. 2 diesel oil	0.842	2.9	6.0	4.8	7.7	13.5	39.0	26.1
No. 6 fuel oil	0.899	5.3	2.3	7.1	6.4	13.3	44.8	20.8
Lummus 3LCF9	1.041	20.3	6.6	16.4	9.0	20.0	16.6	11.1
Lummus 3LCF7	1.022	13.2	6.6	15.8	0.6	23.2	19.5	13.2
Wilsonville Run 255	0.931	7.5	5.2	13.6	8.8	19.2	29.5	16.2
Cresylic acid	-	1.9	24.5	7.4	35.5	4.5	12.5	5.3

TABLE 3

CONDITIONS AND RESULTS OF SUCCESSFUL AGGLOMERATION TRIALS

Run No.	Feed Coal	Agglom. Oil	Slurry pH, Initial/ Final (Agent)	Notes	Added Oil at Phase Inversion/ Total, ml	Product			MF Reject		Organic Recov., %	Ash Rejec- tion, %	Ash Bal., %
						Moisture, wt %	MF Ash, wt %	Air Dry Mass, g	Mass, g	Ash, wt %			
5	Pittsburgh	Diesel	6.1/10.0 (NaOH)	-	3/14	6.58	9.12	105.32	30.76	55.7	86.7	72.2	81.0
6	Pittsburgh	Diesel	6.1/8.5 (NaOH)	1	3/30	8.75	8.97	135.18	38.92	60.9	88.7	65.7	107.9
8	Pittsburgh	3LCF9	8.4/8.4	-	10/35	3.24	8.37	119.99	38.90	50.2	84.8	69.9	90.7
9	Kemmerer	3LCF9	7.3/7.3	-	8/14	14.2	2.83	134.38	0.71	64.2	99.8	10.4	102.1
11	Kemmerer	Diesel	7.3/7.3	-	8/22	10.3	2.62	126.65	1.18	81.1	99.8	18.3	107.9
20	Rosebud	3LCF9	6.3/6.3	-	7/25	8.56	6.05	130.16	0.11	52.9	100.0	-0.9	101.7
21	Rosebud	3LCF9	6.3/6.3	-	7/15	9.69	6.20	122.33	0.18	71.5	100.0	4.0	97.8
22	Wyodak coarse	3LCF9	5.2/5.2	-	13/25	9.83	6.02	131.60	0.18	62.0	99.9	9.2	92.2
26	Wyodak coarse	3LCF7	5.2/5.2	-	10/13	18.2	6.62	131.23	0.61	67.3	99.8	9.7	95.5
27	Wyodak coarse	#6 fuel	5.3/5.3	-	9/10	10.7	7.50	115.97	0.29	90.0	100.0	1.3	102.0
23	Wyodak fine	3LCF9	5.1/5.1	-	15/45	8.56	5.48	156.40	0.52	74.0	99.9	5.9	98.8
29	Wyodak fine	#6 fuel	5.2/5.2	-	10/25	21.7	5.66	159.03	1.14	77.4	99.8	15.4	95.3
36	Wyodak fine	3LCF9	5.1/5.1	2	21/21	12.8	5.76	133.89	2.43	25.4	98.4	19.2	88.2
37	Wyodak fine	Run 255	5.1/5.1	2	20/20	12.0	6.06	129.65	2.09	30.8	98.7	17.0	90.8
28	Texas lignite	#6 fuel	7.1/7.1	-	20/23	19.7	8.19	132.20	6.09	91.4	99.5	39.0	100.0
30	Texas lignite	#6 fuel	6.8/6.8	-	15/15	11.4	7.77	111.56	6.59	91.8	99.4	46.2	96.3
31	Texas lignite	#6 fuel	6.8/2.0 (HCl)	-	15/15	28.6	6.67	131.32	4.44	93.2	99.7	56.2	72.9
33	Texas lignite	#6 fuel	6.7/6.7	2	15/15	22.9	8.73	121.87	5.73	81.6	98.9	42.5	90.3
35	Texas lignite	Run 255	6.7/6.7	2	16/16	11.2	8.78	112.13	5.54	78.6	98.7	38.7	91.8

*Runs conducted at ambient temperature with diesel, 3LCF7 and 3LCF9 oils. Runs conducted at 38°C with Run 255 oil and 54°C with fuel oil #6.
Note 1: 25 g coal added after final oil addition.
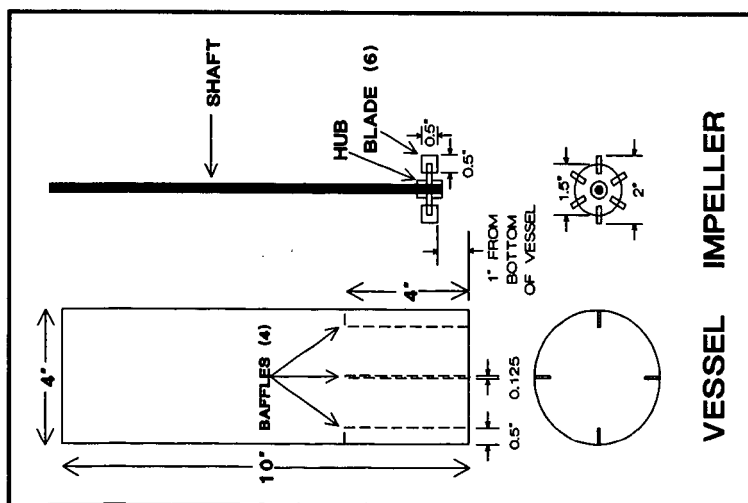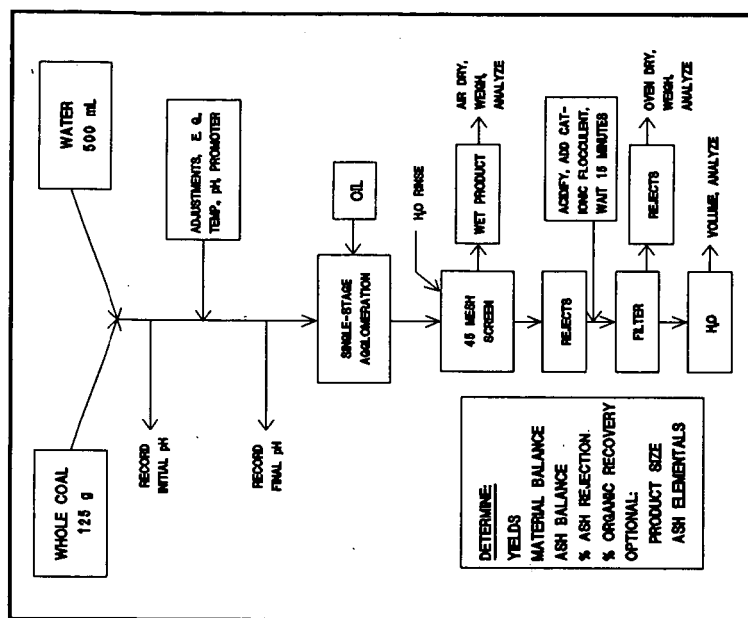Note 2: Promoted by 1.87 g cresylic acid.

Figure 2. Agglomeration Test Procedure.

Figure 1. Apparatus for Bench-Scale Agglomeration Tests.
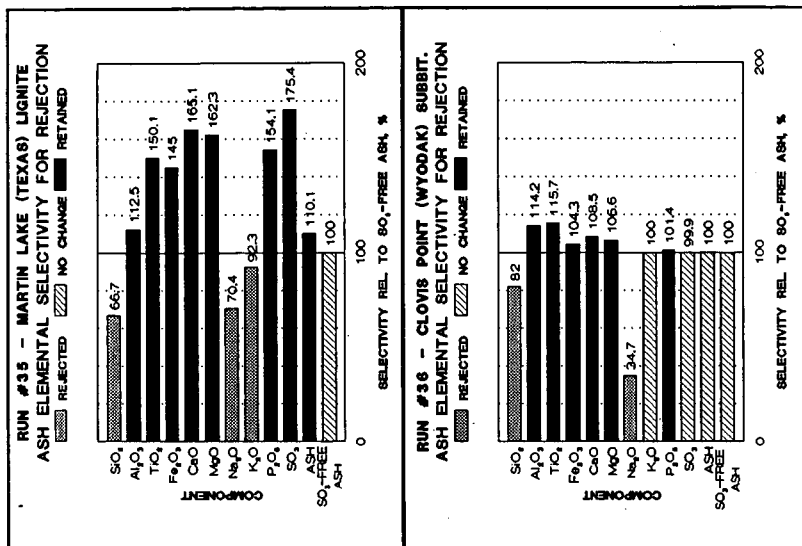
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Figure 4. Ash Elemental Selectivity for Rejection for Selected Runs.
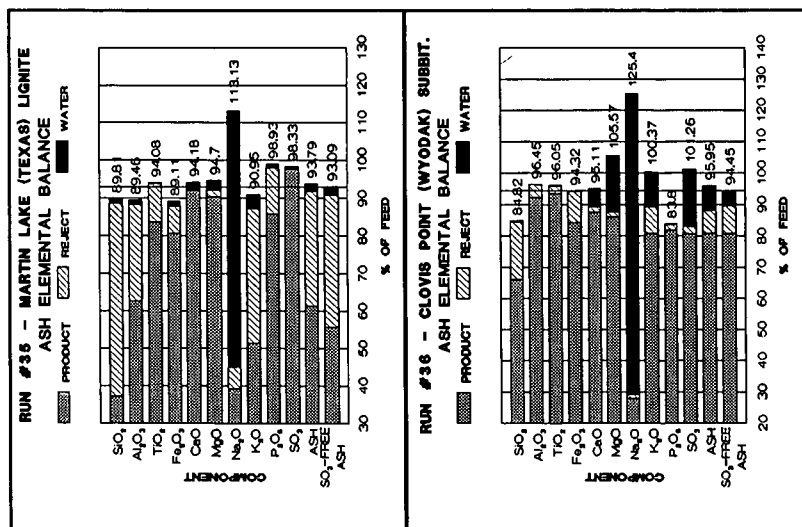
Figure 3. Ash Elemental Balance for Selected Runs.

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